QUALITY ASSURANCE PROJECT PLAN

EPA Region 5 VOC Sampling Method Comparison
Version 1.1

Prepared by:

Motria Caudill
U.S. EPA Region 5
Air and Radiation Division

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SECTION A – PROJECT MANAGEMENT

A.1 Title of Plan and Approval

Quality Assurance Project Plan
EPA Region 5 VOC Sampling Method Comparison

_____Date: _____
Motria Caudill, US EPA Region 5, Project Manager / Principal Investigator

_____Date: _____
Bilal Qazzaz, US EPA Region 5, Quality Assurance Coordinator

_____Date: _____
Loretta Lehrman, US EPA Region 5, Quality Assurance Manager

A.2 Table of Contents

A.3 Distribution List

Motria Caudill, USEPA Region 5 Air & Radiation Division (ARD)

Wayne Whipple, USEPA Region 5 Chicago Regional Laboratory (CRL)

Karen Oliver, USEPA Office of Research and Development (ORD)

Chad McEvoy, USEPA Region 5 ARD

Anthony Ross, USEPA Region 5 ARD

Bilal Qazzaz, USEPA Region 5 ARD

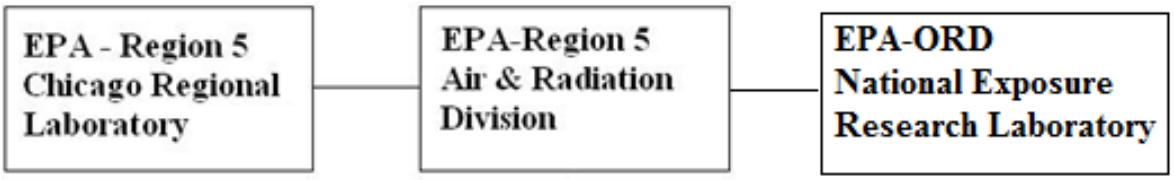
Loretta Lehrman, USEPA Region 5 ARD

A.4 Project/Task Organization

Table A.1 Roles & Responsibilities

Individual Assigned	Responsible for:	Authorized to:
Motria Caudill	• Principal Investigator • QAPP revisions, data analysis, report preparation	• Communicate findings to EPA Region 5, EPA ORD, and MECAP
Wayne Whipple	• Laboratory Analysis • Laboratory QC	• Analyze samples
Karen Oliver	• Laboratory Analysis • Laboratory QC	• Analyze samples
Chad McEvoy	• Field Operations • QC on field sampling	• Collect, document, ship samples
Bilal Qazzaz	• QAPP review • Data validation	• Determine whether DQOs are met
Loretta Lehrman	• QAPP approval • Data package approval	• Manage EPA R5 AMAS staff assignments and travel

Figure A.1 Organization Chart



A.5 Problem Definition/Background

This study is part of a broader evaluation of a low-cost passive VOC sorbent tube sampler which was developed by EPA-ORD. The study involves interaction with multiple EPA Regions (Regions 3, 5, 6, and 8) under the RARE Program. The project has a number of objectives including technology transfer, evaluation of sampler precision, concentrations from a range of source impacts, assessment of analytical results from EPA ORD and multiple commercial laboratories in a laboratory intercomparison, and collocation of collocated VOC canisters. The results from this project may be useful to the EPA Regions and Program Offices for evaluating VOC concentrations in urban areas and near air pollution sources, however, the quality assurance category for this project is not appropriate for regulatory, enforcement, or compliance activity. This project may also provide useful information to the Office of Air Quality Planning and Standards for evaluating the application EPA Draft Method 325A/B which uses passive sampling to quantify Benzene. The Region staff will provide information on the deployment of samplers and the laboratory intercomparison may provide information on whether commercial laboratories meet analytical performance requirements. Participating EPA Regions have each selected monitoring sites and designed sampling studies to evaluate a range of source types. ORD will analyze the samples from the regions and also lead the laboratory intercomparison evaluation of the commercial laboratories.

The central component of this study – passive VOC sorbent tube sampling – is detailed in the QAPP titled "Collaborative Evaluation of a Low-Cost Volatile Organic Compounds Passive Sampling Method and Analytical Laboratory Intercomparison", updated March 1, 2014.

In conjunction with the multi-Regional sorbent tube study, limited canister sampling will be conducted to test the accuracy of the new method. Once the multi-Region RARE effort is complete, Region 5 will continue to collect additional paired samples of sorbent tubes and canisters in order to develop a robust method comparison dataset. The ultimate aim is to collect and analyze 25 paired samples for sorbent tube and canister comparison.

A.6 Project/Task Description

Passive sorbent tubes with Carbopack X® sorbent material have been deployed successfully for monitoring of VOCs during previous EPA ORD studies. The passive sorbent tubes utilized for the current study are constructed of passivated stainless steel, are 89 millimeters long, and are packed with Carbopack X® sorbent material. Passive tube sample collection will follow the EPA-ORD "Standard Operating Procedure for

Carbopack X Sorbent Tube Handling: Field Deployment and Shipping", which is included as Appendix D to the aforementioned multi-Regional study QAPP.

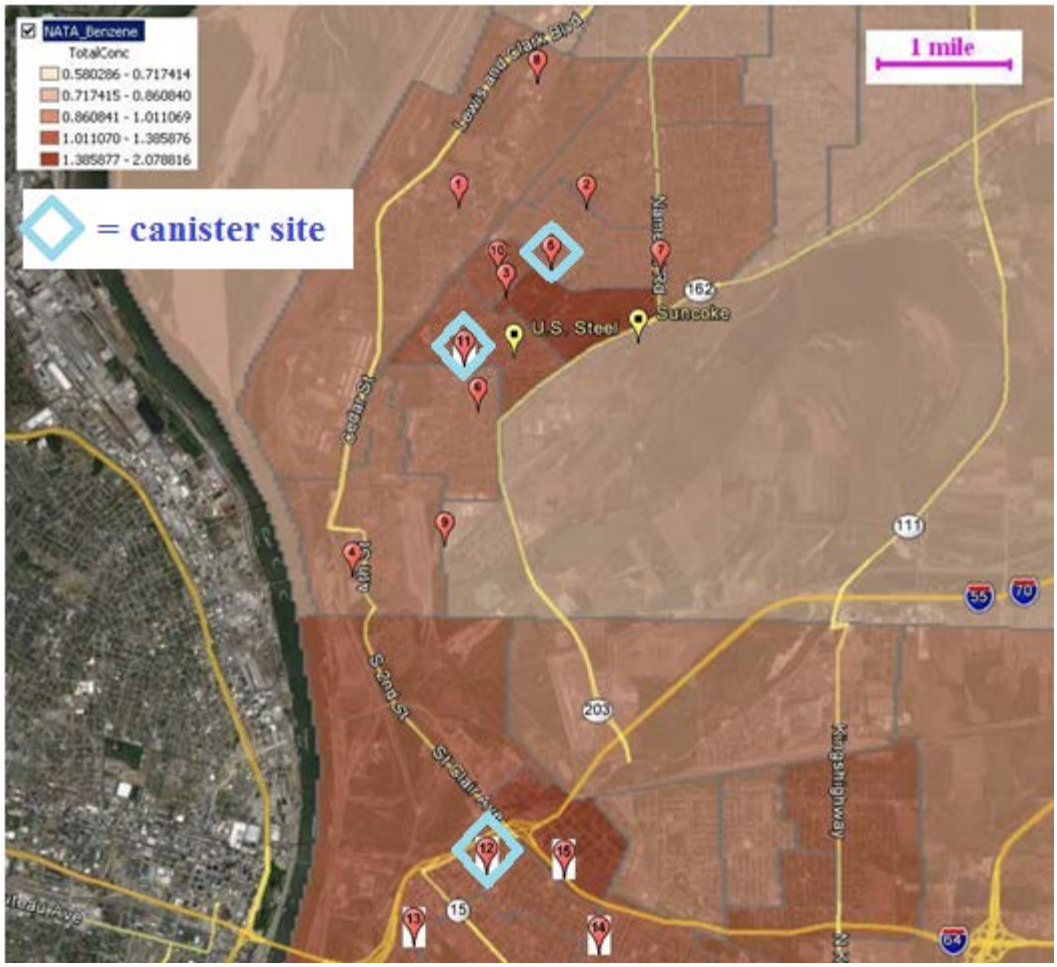
The passive sorbent tubes will be deployed in EPA designed and supplied sampling shelters. The samples will be collected at locations following siting criteria determined appropriate by the multi-Region RARE study and consistent with guidelines in EPA Draft Method 325A. Collocated canister samples will be deployed with inlets less than two meters away from passive tubes.

The Region 5 component of the RARE study involves collecting 1-week long integrated samples in three distinct field campaigns in Granite City and East Saint Louis, IL. A second phase of sampling will be conducted in Whiting, Indiana, at fenceline monitoring stations established by BP Whiting.

A.6.i Sampling in Granite City and East Saint Louis, IL

A site map is presented on Figure A.2.

Figure A.2. Illinois Sampling Sites and Predicted Ambient Benzene Concentrations (ug/m^3)



The area of Granite City, IL and East St. Louis, IL, is heavily impacted by industrial and mobile-source emissions. The ambient air quality monitoring network operated by Illinois EPA includes criteria pollutant

and toxics metals stations. However, VOCs have not historically been monitored in these communities and the concentrations may be elevated near various metallurgic industries, coke producers, and areas of dense on-road vehicle emissions. NATA-predicted benzene concentrations are similarly elevated in East St. Louis at the confluence of interstate highways 70, 55 and 64, at the point where vehicle traffic crosses between Illinois and Missouri over the Mississippi River.

To assist in characterizing the range of VOC concentrations throughout the Granite City and East St. Louis area, a saturation study will be conducted. In this saturation study, passive sorbent tubes will be deployed throughout the community at varying distances from major industrial sources and at locations where dense mobile source emissions are expected. This project has two internal objectives and the data could be used by the Region to characterize typical ambient concentrations of VOCs in the area and define spatial gradients for individual compounds. The results of this saturation study will be compared to reference sites in the Midwest, including long-term VOC trends stations in St. Louis, MO, Chicago, IL, Gary, IN, and Milwaukee, WI. Determinations made from the study could potentially lead to the initiation of long-term VOC monitoring in greater East St. Louis and could inform ideal placement of a new monitoring station.

Fifteen sites have been selected for the saturation study throughout the Granite City and East St. Louis, IL area. The majority of the sites were selected from a previous MECAP community-based nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) passive monitoring study. These sites are well distributed in the community and are placed at varying distances from different industrial point sources and mobile emissions sources. In many urban and industrial communities, the most significant health risks from VOCs are attributed to benzene. The study community is known to have significant local emissions from coke ovens, metallurgic facilities, and various on-and off-road mobile sources. Study sites were chosen with greatest consideration to areas where ambient benzene concentrations are likely to be elevated.

Of the fifteen passive tube sampling sites, a subset of three were chosen for canister collocation. All site descriptions are shown below on Table A-2 with an indication of which locations include passive canister collection.

Each canister sample will consist of one Summa canister attached to a critical orifice. The orifice will restrict the flow so that when the canister (starting under vacuum) is opened it will slowly fill over a 1-week period of time. A field operator will manually open and close each canister, documenting sample location, time canister open, time canister closed, and make observations about site conditions and meteorology.

Samples will be logged on a chain of custody form, and the form and samples will be sent to EPA-CRL. The samples will be analyzed using method TO-15 for VOCs.

Table A-2. Sampling Site Descriptions

ID	Tube	Canister	Address	City	Type of Location
1	X		2402 Illinois Ave	Granite City	Residence
2	X		1350 27th St (moved to 2723 Michigan Ave.)	Granite City	Residence
3	X		2014 State Street	Granite City	Labor Temple
4	X		206 Kerr St	Venice	Community Garden
5	X	X	2300 Madison Avenue	Granite City	Firehouse
6	X		1000 Alton Ave	Madison	Residence
7	X		Nameoki Rd & East 24th St	Granite City	Community Garden
8	X		4 Konzen Court	Granite City	Empty City Lot
9	X		904 Grand Avenue	Madison	Residence
10	X		2101 Cleveland Blvd	Granite City	Church Community Garden
11	X	X	15 & Madison Ave	Granite City	IEPA Monitoring Station
12	X	X	North 6th St	East St. Louis	Christian Activity Center
13	X		601 James R Thompson Blvd	East St. Louis	East St. Louis Higher Education Center
14	X		638 N 20th St	East St. Louis	Eastside Health District, Public Health
15	X		1435 Baugh Ave.	East St. Louis	Metro Link

The first round of sorbent tube sampling occurred in September 2013. Canister sampling will be added to the second and third rounds of the study, which are scheduled to begin respectively on November 5th and December 3rd, 2013.

A.6.ii Sampling at BP Whiting Refinery Fenceline Stations, Whiting, IN

An agreement was made in 2012 between the BP Whiting Refinery, local environmental agencies, and private citizen groups to provide air quality information to the public. BP is providing comprehensive air quality information regarding conditions at the refinery, as measured at four fenceline stations (see Figure A.3) each equipped with an auto-GC system and open-path instruments for VOC monitoring.

Fixed monitoring station locations:

- Site 1 Southwest near the intersection of Schrage Avenue and 129th Street
- Site 2 West near the intersection of Indianapolis Blvd and Schrage Avenue
- Site 3 Northwest near the intersection of Schrage Avenue and 121st Street
- Site 4 Southeast at the intersection of Dickey Road and 129th Street

Figure A.3. BP Refinery Whiting, Indiana Sampling Sites

Back-to-back weekly samples will be collected every Thursday morning for a six-week period beginning on August 21st. A full set of samples will consist of one passive tube and one canister collected at each of the four fixed fenceline stations.

A.7 Quality Objectives & Criteria

The purpose of VOC canister sampling is to determine whether pollutant concentrations are approximately the same as collocated samples from passive sorbent tubes. Canisters analyzed in Region 5 and tubes analyzed at ORD will report the same parameter list with comparable detection limits.

The resulting data will be considered of sufficient quantity and quality if minimum detection limits MDLs are 35 pptv for the twenty-five compounds listed below:

1,2-Dichloro-1,1,2,2-tetrafluoroethane
1,3-Butadiene
Trichlorofluoromethane
1,1-Dichloroethene
1,1,2-Trichloro-1,2,2-trifluoroethane
1,1-Dichloroethane
cis-1,2-Dichloroethene
1,2-Dichloroethane
1,1,1-Trichloroethane
Benzene
Carbon tetrachloride
1,2-Dichloropropane
Trichloroethene
Toluene
Tetrachloroethene
Chlorobenzene
Ethylbenzene
m,p-Xylene
Styrene
o-Xylene
4-Ethyltoluene
1,3,5-Trimethybenzene
m-Dichlorobenzene
p-Dichlorobenzene
o-Dichlorobenzene

A.8 Special Training/Certification

EPA Region 5 field staff and U of IL field personnel have been trained on passive tube and canister collection protocols. EPA staff who will participate in sampling at BP Refinery will be required to watch a safety video and pass a written test before entering the site.

A.9 Documents and Records

The principal investigator (PI) will have responsibility to ensure all QAPP revisions are shared with project participants. Each revision of the QAPP will be numbered and dated.

Each sample collected will be numbered, date and time sample collection started and ended, initial and final gauge reading, site name or location, and sample collection. Each sample will have a sample tag that will accompany each sample to the lab. A chain of custody form will accompany each batch of samples.

The PI will create a database for the sample results which will be used during data analysis. This database will be archived and retained for 5 years.

The PI will write the final report, which will summarize the details of the samples collected, the results of the analysis of those samples, outline the analysis performed, and the final conclusions/recommendations.

SECTION B – DATA GENERATION & AQCUISITION

B.1 Sampling Process Design (Experimental Design)

Passive canister sampling will coincide with 1-week long sorbent tube deployments in Granite City, IL, in November and December, 2013. Out of fifteen tube sites, a subset of three locations was selected for canister sampling. Additional paired samples (canister and tube) will be collected at the four fenceline air monitoring stations at BP Refinery Whiting, Indiana.

B.2 Sampling Methods

Each sample will consist of one Summa canister attached to a critical orifice and one passive sorbent tube. The canister orifice will restrict the flow so that when the canister (starting under vacuum) is opened it will slowly fill over a one-week period. The sorbent tube will be uncapped and the canister opened in immediate succession; both will be closed at the same time approximately one week later. A field operator will manually open and close each canister, documenting sample location, date and time canister is opened and closed, initial and final gauge vacuum, and local observations.

Canister samples will be logged on a chain of custody form, and the form and samples will be sent to EPA-CRL within one week of collection. The samples will be analyzed using method TO-15 for VOCs. Passive tubes will be sent to EPA-ORD.

B.3 Sampling Handling & Custody

Physical air samples for VOCs will be collected in canisters which have been cleaned and evacuated according to strict SOPs. EPA-CRL has developed and qualified SOPs for the TO-15 analytical method. Chain of custody forms will accompany the canisters to and from the lab and will be completed by the field staff as the samples are collected.

B.4 Analytical Methods

Method TO-15 will be used to analyze canister samples. EPA-CRL has SOPs in place for this method. Passive tubes will be analyzed by EPA-ORD with methods detailed in the QAPP titled "Collaborative Evaluation of a Low-Cost Volatile Organic Compounds Passive Sampling Method and Analytical Laboratory Intercomparison", updated March 1, 2014.

B.5 Quality Control

Consistent with other air toxics monitoring networks, this study will include collocation of 25% of ambient canister samples. To meet this requirement, one in four canisters should be collected in duplicate. As noted in Section A.7, the duplicate samples should have a coefficient of variance (precision) of equal to or less than 30% for benzene.

Evaluation of Collocated Data- All collocated data will be reported to AQS. The following algorithms will be used to evaluate collocated data. Collocated measurement pairs are selected for use in the precision calculations only when both measurements are within the acceptance criteria.
The percentage difference, d_i, for each check is calculated by using the following equation, where X_i represents the concentration produced from the primary sampler and Y_i represents the concentration reported for the duplicate sampler.

$$\frac{d_i = Y_i - X_i \times 100}{(Y_i + X_i)/2}$$

Estimate of Precision - In 2008, the EPA changed the calculations that derive precision, i.e., precision is expressed as coefficient of variance (CV). The following equation is used to calculate the CV. The precision estimate is used to assess the one-point QC checks for gaseous pollutants described in section 3.2.1 of CFR Part 58, Appendix A1. The precision estimator is the coefficient of variation upper bound and is calculated as follows:

$$CV = \sqrt{\frac{n \cdot \sum_{i=1}^{n} d_i^2 - \left(\sum_{i=1}^{n} d_i\right)^2}{n(n-1)}} \cdot \sqrt{\frac{n-1}{\chi^2_{0.1,n-1}}}$$

Where $\chi^2_{0.1,\,n-1}$ is the 10th percentile of a chi-squared distribution with *n-1* degrees of freedom.

B.6 Instrument/Equipment Testing, Inspection, and Maintenance

EPA-CRL will inspect all canisters and orifices prior to sending them to the field; the lab will look for any defects or damage to the equipment, and will ensure all components are clean.

Field operators will inspect all equipment upon receipt, prior to initiating the sample, at sample

collection, and prior to shipping the sample back to the lab. Operators will want to look for damage that occurred during shipping or sampling, and also to look for cleanliness of the equipment, especially the inlets of the orifices.

Field operators should also take care that the orifices are not cross-threaded when attaching the summa canister. The operators will also want to ensure that the connection is tight.

Any problems with the orifices or canisters should be documented and communicated to the lab and the principal investigator.

B.7 Instrument/Equipment Calibration and Frequency

No measurement equipment will be used in the field; the Summa canisters and sampling orifices do not require calibrations.

B.8 Inspection/Acceptance of Supplies & Consumables

Upon receipt of the Summa canisters U of IL staff will visually inspect the canisters to look for any damage that may have occurred during shipping.

B.9 Data Management

Record keeping begins when the samples leave the lab and go to the field collectors. Field staff will record information about the sample (dates, time, etc) and continue filling in the chain of custody. The samples and information will go back to the lab, and the samples will be analyzed. The QA Manager will then quality assure the data, ensuring that the data is valid, and then pass the data on to the principle investigator. The PI will then consolidate the results into a database for analysis. This data, and the analysis, will be included in the final report.

In addition to the data files that will be kept for this project, records that will be kept will include the following:

1. Field Logbooks –used to record field activity, including but not limited to sample collection (canister/orifice numbers, start/stop dates and times, gauge vacuum, sampling location, local observations, etc)

2. QAPP and SOP – a copy of this QAPP and SOPs will be available at all times.

SECTION C – ASSESSMENT AND OVERSIGHT

C.1 Assessments and Response Actions

An assessment is defined as an evaluation process used to measure the performance or effectiveness of the quality system or the establishment of the monitoring network and sites and various measurement phases of the data operation. The results of quality assurance assessments indicate whether the control efforts are adequate or need to be improved. Documentation of all quality assurance and quality control efforts implemented during the data collection, analysis, and reporting phases is important to data users, who can then consider the impact of these control efforts on the data quality. In order to ensure the adequate performance of the quality system, the following assessments will be performed:

- Performance Testing (PT) to assess the EPA laboratory conducting VOC analyses. The laboratory will analyze one PT sample collected via the Region 5 Laboratory Inter-comparability program near the beginning of the program and a second one at the end.

- Network siting and review. The EPA QA Manager reviewed siting criteria for all sample locations prior to the beginning of the program.

C.2 Reports to Management

The principal investigator (PI) will summarize data results monthly and will write the final report. The monthly summaries will address performance evaluation and audits, as well as data quality assessments. The final report will consolidate QA findings and address the primary study questions. The PI will provide monthly and final reports to management within U.S. EPA Region 5 and Illinois EPA.

SECTION D – DATA VALIDATION AND USABILITY

D.1 Data Review, Verification, and Validation

Prior to performing any statistical calculations, the reported data from the chain of custody forms are checked to ensure accurate transcription.

D.2 Verification and Validation Methods

At least 10% of the database is checked to verify its validity. Items checked include original data sheets, checks of all calculations (from calibration to sample analysis), and data transfers. As the data are checked, corrections are made to the database as errors or omissions are encountered. If errors are located, all of the data is checked to verify data quality. Documentation of equipment and instrument calibration and other procedures are detailed in the laboratory's SOPs.

D.3 Reconciliation with User Requirements

Per the DQOs in Section A.7, data will be rejected if MDLs for benzene are not met. The PI will conduct a preliminary data review to uncover potential limitations to using the data, to reveal outliers, and generally to explore the basic structure of the data. The first step is to calculate basic summary statistics, generate graphical presentations of the data, and review these summary statistics and graphs. The PI will calculate statistics for VOC completeness and precision. Data will be qualified and used if criteria for completeness and precision are not met.

Appendix A

Standard Operating Procedure, VOC canister sample collection

Standard Operating Procedure

Setting-Up Passive Canisters for Volatile Organic Compounds

US EPA Region 5 Air and Radiation Monitoring and Analysis Section (AMAS) and

University of IL, Metro East Community Air Project (MECAP)

October 30, 2013

DRAFT 1.0

1. Canisters will be shipped from EPA-CRL to the MECAP office:

   Amy Funk, Project Coordinator
   Metro East Community Air Project
   1 Regency Plaza Drive
   Collinsville, IL 62234
   Tel. 618-514-7854
   amyfunk@illinois.edu

   MECAP staff should inspect the canisters for possible damage that may have occurred during shipping. Canisters should be used within 30 days of receipt from the lab.
2. To set-up a canister to collect a sample, the operator should take several canisters, orifices/regulators, labels, chain of custody forms, wrenches, zip ties, the field log book, and a time-piece to the field. It is recommended that spare components go to the field in the event there is a problem with any of them. The field operator should attempt to avoid contaminating the sample by not interacting with sources of VOCs prior to handling the canister.
3. At the site, enter relevant information for the sample on the sample label **AND** the log book. Duplicate information entries are helpful should the sample label be lost or destroyed. Relevant information is the field collector's name, canister number, orifice number, site name/location, sample date, and sample time. Information should also be entered onto the Chain of Custody form.
4. Using a wrench, remove the sample cap and attach the orifice to the canister. Take care to not cross-thread the fittings while connecting them.
5. Attach the canister/orifice assembly to the sample support (ie sign-post, fence, etc).
6. Open the valve of the canister (usually the green knob at the top of the canister and labeled with "open" and "close"). Note and record the initial canister vacuum from the orifice gauge on both the sample label and log book (typical vacuum for a canister will be around 30 inches mercury. Consider using a different canister if vacuum is 25 inches or less). Also note any relevant local observations (possibilities include weather conditions, road work, landscaping, painting, etc).
7. Return to collect the canister before 24 hours have elapsed. The canister's orifice is set at a flow rate that should fill the canister in about 24 hours. It is desired that the canister not reach ambient pressure and remain open; this would allow air to freely diffuse in and out of the canister and not represent a 24 hour sample time.
8. Close the valve on the orifice and remove the canister/orifice assembly from the sample support (ie sign-post, fence, etc).
9. Note and record the final canister vacuum from the orifice gauge on both the sample label and log book. Also note any relevant local observations (possibilities include weather conditions, road work, landscaping, painting, etc). Also complete the chain of custody form.
10. Affix the sample label to the canister, and remove the orifice from the canister with a wrench. Place the cap on the canister to seal it. Examine the orifice to ensure no debris has collected around the orifice opening. If it is dirty, wipe it clean or contact the lab for additional assistance.
11. Pack the canister and chain of custody for shipping back to the lab. Samples should be returned to the lab within a week. Shipping address is:

    Central Regional Laboratory
    Attention: Rob Schneider
    536 S. Clark St. 10th Floor
    Chicago, IL 60605

12. Analysis results will be sent to both AMAS and MECAP.

Appendix B

Standard Operating Procedure, VOC passive tube sample collection

Appendix C

BP Refinery Whiting – URS Fenceline Air Monitoring – Safe Work Plan